

Kinetics and Thermodynamic Studies on the Adsorption of Co^{2+} onto Chitosan-aluminium Oxide Composite Material

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Abstract

Kinetics and thermodynamic on the adsorption of Co^{2+} onto chitosan-aluminium oxide composite material were studied, and the kinetics and thermodynamics equations, activation energy (E_a), and the thermodynamics constant were obtained. The adsorption of Co^{2+} onto chitosan-aluminium oxide composite material was found to follow pseudo-second-order kinetic model.

Keywords: Chitosan, Composite material, Adsorption, Kinetics, Thermodynamics

1. Instruction

Chitosan is a linear polysaccharide composed of randomly distributed β -(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine. It has high adsorption capacity for a variety of heavy metals including cobalt, copper, and mercury (Majeti & Ravi, 2000; Chu, 2002; Burke et al., 2002; Dhakal et al., 2005). Furthermore, chitosan can be easily synthesized through chitin deacetylation with low cost. These two characteristics make chitosan an excellent candidate for manufacturing commercial adsorbent for wastewater treatment and heavy metal enrichment and recycling (Mayumi et al., 2004; Veera et al., 2003). Yet, as an organic compound, chitosan has poor sulfuric acid resistance and weak mechanical strength, thus limiting its commercial applications. In addition, the presence of large amount of hydrogen bonding within chitosan could decrease its adsorption capacity. Aiming to overcome these limitations, it has been demonstrated that synthesis of chitosan-inorganic composite material can be a promising approach for the design of new chitosan adsorbents. For example, Xie et al. (Xie & Du, 2009) prepared the chitosan-aluminium oxide composite material using chitosan and isopropanol aluminum and found that the adsorption capacity of such composite towards copper ions and mercury ions had been greatly improved.

In this study, we focus on a better understanding towards the fundamental aspects of the adsorption of heavy metal such as cobalt onto chitosan-aluminium oxide composite and present a thorough kinetic and thermodynamic investigation of the adsorption process. We hope our results can provide valuable insights for a better design of chitosan-inorganic composite materials.

2. Experimental

2.1 Reagents

All reagents, except chitosan, were of analytical reagent grade. Chitosan (> 90%) was purchased from Zhejiang Golden-shell Biochemical Co., Ltd., China. Isopropanol aluminum (> 99.5%) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (> 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. China. Toluene (AR), Ethanol (AR).

2.2 Experimental methods

Chitosan-aluminum oxide composite material was prepared according to the procedure described in previous study (Xie et al., 2009). Briefly, 3 g of isopropanol aluminum was added into 100 ml of toluene in a three-neck

bottle equipped with reflux condenser. The mixture was kept at 323 K under nitrogen protection and was stirred for 30 min. 10 g of chitosan was then added into the mixture and the mixture was kept at 385 K for 5 h. The crude product first went through leaching and washing with toluene, ethanol, and distilled water, and then dried at 353 K in an oven.

Adsorption experiments were carried out in a flask placed in a water bath oscillator. 0.5000 g composite material was added into $\text{Co}(\text{NO}_3)_2$ solution to carry the adsorption study. The oscillator oscillated at 130 r/min. Take the filtrate by UV-VIS spectrophotometer to measure absorbency values at 512 nm place (why UV-vis, please give more details). Adsorption was calculated according to equation (1).

$$Q = (C_0 - C) \times V / m \quad (1)$$

Where Q is adsorption capacity, C_0 and C are the initial concentration and the final concentration of Co^{2+} , V is the solution volume, and m is the adsorbent mass.

3. Result and discussion

3.1 Kinetic studies on the adsorption of Co^{2+} onto chitosan-aluminum oxide composite material

Fig. 1 shows the adsorption kinetic curve of Co^{2+} onto the chitosan-aluminum oxide composite material at different temperatures. The results demonstrated that the composite material had good adsorption properties towards Co^{2+} . This adsorption procedure was generally consistent with the three-step adsorption behavior usually observed from porous adsorbents (Huang et al., 2009). Initially, the adsorption rate was fast, and then decreased over time, after about 480 minutes, the adsorption reached equilibrium. At the beginning, the adsorption of Co^{2+} onto composite material mainly occurred on the external surface of composite material and the adsorption rate was rapid. Then the concentration of Co^{2+} began to decrease over time. This is because that adsorbed cobalt ions diffused inward into the composite material through the micropore, and the resistance of diffusion increased with adsorption procedure. Adsorption rate was mainly controlled by diffusion at this stage, so the rate of adsorption then becomes small. At the final stage, the adsorption mainly occurred on the inner surface of adsorbent and the adsorption reached equilibrium at the last stage.

Pseudo second order kinetics model was used to fit the kinetic data. This model is based on assumption of that: the rate of adsorption is determined by the square of the number of vacancies (Sun et al., 2009). The formula is:

$$dQ_t/dt = k (Q_{eq} - Q_t)^2 \quad (2)$$

Integration of equation (2) under boundary conditions resulted in equation (3)

$$t/Q_t = t/Q_{eq} + 1/kQ_{eq}^2 \quad (3)$$

Where Q_t ($\text{mmol}\cdot\text{g}^{-1}$) is the adsorption amount at time t (minute); and Q_{eq} ($\text{mmol}\cdot\text{g}^{-1}$) is the adsorption amount at equilibrium; k ($\text{g}\cdot\text{mmol}^{-1}\cdot\text{min}^{-1}$) is the adsorption rate constant.

If adsorption procedure conforms to pseudo-second-order equation, t/Q_t and t could have a linear relationship. Indeed, fitting the data in fig. 1 resulted in a straight line, as shown in fig. 2.

Temperature study ($\ln k$ versus $1/T$, fig3.) showed a R^2 value of 0.9912. This indicated that the relationship between temperature and the rate of adsorption obeyed the Arrhenius equation

$$\ln k = -E_a/RT + \ln A \quad (3)$$

The temperature had significant effect on the rate constant k. According to the Arrhenius equation, the obtained E_a was $14.64 \text{ kJ}\cdot\text{mol}^{-1}$. This further proved our previous hypothesis that the adsorption procedure was chemical adsorption.

3.2 Thermodynamic studies on the adsorption of Co^{2+} onto chitosan-aluminium oxide composite material

Fig. 4 showed that the adsorption capacity of Co^{2+} on the composite material increased with the increase of the initial concentration of Co^{2+} in solution, and then it reached a maximum value. This was due to that the amount of composite material was at a fixed value and thus the number of adsorption sites was at a fixed value too. At the beginning of the adsorption, the composite materials could provide enough sites, thus the adsorption capacity of composite materials was high (Cheng et al., 2009); however, the active sites became insufficient when the initial concentration of Co^{2+} was high and the adsorption sites could be saturated under such situation.

The expression of the Freundlich adsorption model is listed below.

$$\lg Q_{eq} = 1/n \lg C_{eq} + \lg K_F \quad (4)$$

Where, C_{eq} and Q_{eq} are the equilibrium concentration of metal ions ($\text{mmol}\cdot\text{L}^{-1}$) and the adsorption capacity ($\text{mmol}\cdot\text{g}^{-1}$), respectively; $1/n$ is Freundlich constant; K_F is the equilibrium constant.

From Table 2, we can see that the adsorption of Co^{2+} onto the composite material was consistent with the Freundlich model. This suggested that the adsorption procedure was consistent with a multimolecular layer adsorption model.

The relationship between K_f and T can be obtained from the Van't Hoff equation (Atia et al., 2006).

$$\ln K_f = -\Delta H^\circ/RT + \Delta S^\circ/R \quad (5)$$

Where ΔH° ($\text{J}\cdot\text{mol}^{-1}$) and ΔS° ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) are the enthalpy of adsorption and the entropy of adsorption, respectively; R is the ideal gas constant; T (K) is temperature. $\ln K_f$ had a linear relationship with $1/T$ with a R^2 value of 0.9720. The slope and intercept are $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively. And ΔH° and ΔS° were determined to be $1.610 \text{ kJ}\cdot\text{mol}^{-1}$ and $18.46 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively.

The results of ΔG° were listed in Table 3. Gibbs free energy (ΔG°) was negative at all four temperatures. ΔG° decreased with the increase of temperature. It suggested that the adsorption of Co^{2+} on the composite material was a spontaneous procedure. The spontaneous degree becomes greater with the increase of temperature. Therefore, increasing temperature is beneficial to the adsorption procedure.

4. Conclusions

The adsorption kinetics of Co^{2+} onto chitosan-aluminum oxide composite materials was found to follow the pseudo-second-order kinetic model. Adsorption procedure was mainly chemical adsorption, and the apparent adsorption activation energy was measured to be $14.64 \text{ kJ}\cdot\text{mol}^{-1}$. Thermodynamic studies indicated that the adsorption procedure conformed to the Freundlich adsorption model. The adsorption thermodynamic parameters such as ΔH° , ΔS° , ΔG° , were obtained. The adsorption reaction was found to be exothermic.

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Table 1. Adsorption dynamic parameters at different temperatures

T/K	$Q_{eq}/(\text{mmol}\cdot\text{g}^{-1})$	$k/(\text{g}\cdot\text{mmol}^{-1}\cdot\text{min}^{-1})$	R^2
298K	1.032	0.02730	0.9998
308K	1.056	0.03225	0.9998
318K	1.079	0.04057	0.9996
328K	1.116	0.05740	0.9997

Table 2. Parameters and equations for Freundlich adsorption model

T/K	Freundlich equation	n	K_F	R^2
298	$\lg Q_{eq}=0.5936\lg C_{eq}+0.6814$	1.685	4.801	0.9997
308	$\lg Q_{eq}=0.5840\lg C_{eq}+0.6935$	1.712	4.937	0.9998
318	$\lg Q_{eq}=0.5560\lg C_{eq}+0.6977$	1.759	4.985	0.9998
328	$\lg Q_{eq}=0.5574\lg C_{eq}+0.7086$	1.794	5.113	0.9999

Table 3. The results of ΔG° at different temperatures

T/K	298K	308K	318K	328K
$\Delta G^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	-3.887	-4.089	-4.247	-4.450

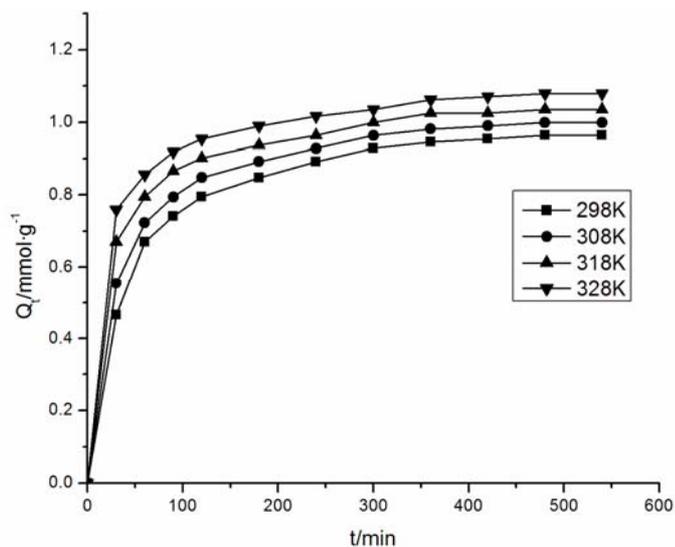


Figure 1. Adsorption kinetic curve

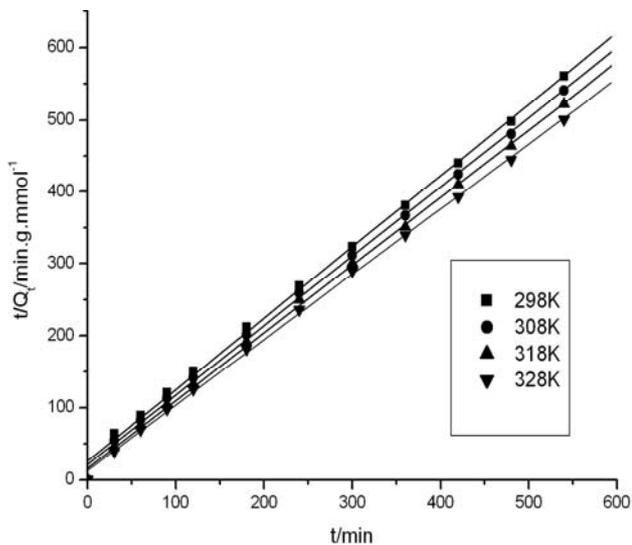


Figure 2. Pseudo Second-order Equation Plots

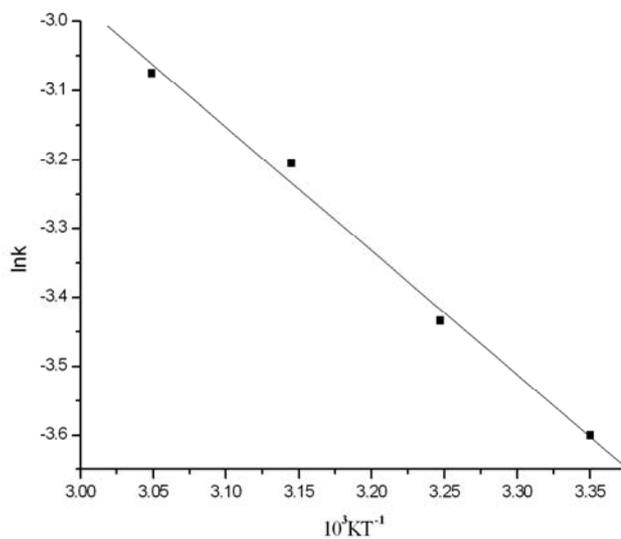


Figure 3. Relationship Between lnk and 1/T

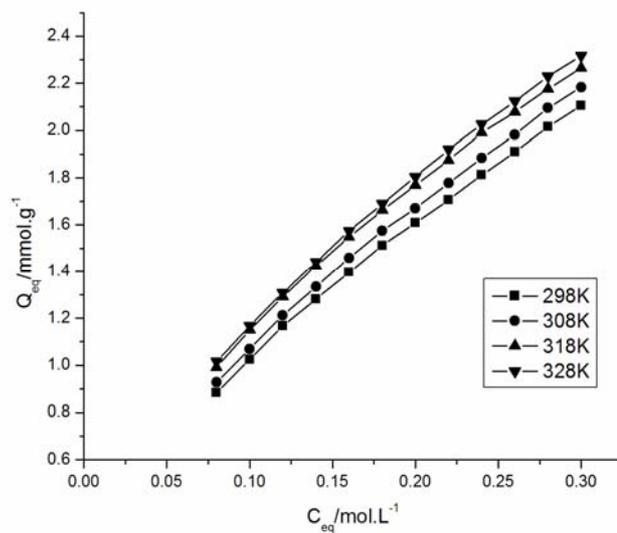


Figure 4. Adsorption capacity of Co^{2+} in Different Temperature